

## Bonding and Structure of Copper Nitrenes

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Copper nitrenes are of interest as intermediates in the catalytic aziridination of olefins and the amination of C–H bonds. However, despite advances in the isolation and study of late-transition-metal multiply bonded complexes, a bona fide structurally characterized example of a terminal copper nitrene has, to our knowledge, not been reported. In anticipation of such a report, terminal copper nitrenes are studied from a computational perspective. The nitrene complexes studied here are of the form ( $\beta$ -diketiminato)Cu(NPh). Density functional theory (DFT), complete active space self-consistent-field (CASSCF) electronic structure techniques, and hybrid quantum mechanical/molecular mechanical (QM/MM) methods are employed to study such species. While DFT methods indicate that a triplet ( $S = 1$ ) is the ground state, CASSCF calculations indicate that a singlet ( $S = 0$ ) is the ground state, with only a small energy gap between the singlet and triplet. Moreover, the ground-state (open-shell) singlet copper nitrene is found to be highly multiconfigurational (i.e., biradical) and to possess a bent geometry about the nitrene nitrogen, contrasting with the linear nitrene geometry of the triplet copper nitrenes. CASSCF calculations also reveal the existence of a closed-shell singlet state with some degree of multiple bonding character for the copper–nitrene bond.

## Introduction

Copper catalysts are widely used for nitrene (NR, where R is most often a hydrocarbyl or functionalized hydrocarbyl group) transfer, most notably the aziridination of unsaturated organic substrates such as olefins.<sup>1</sup> For example, Jacobsen and co-workers have suggested that aziridination by copper diimine catalysts involves a copper nitrene intermediate.<sup>2</sup> Brandt et al. clarified the mechanism of the copper-catalyzed aziridination of alkenes through a combination of density functional theory (DFT) calculations and kinetics experiments.<sup>3</sup> In related chemistry, Perez and co-workers have studied the mechanism of alkene aziridination and C–H bond amination by copper scorpionate catalysts.<sup>4</sup> While aziridi-

nation has been widely studied from an experimental point of view, another attractive target is nitrene transfer to CO to yield isocyanates, which are widely used as intermediates for the production of polymers.<sup>5</sup> Several researchers have demonstrated the feasibility of aryl isocyanate (ArNCO) synthesis by the reaction of CO with structurally characterized arylimido/nitrene complexes of late transition metals. For example, Mindiola and Hillhouse have reacted a bis-(phosphine)nickel nitrene with CO to form ArNCO.<sup>6</sup> Bart et al.<sup>7</sup> and Peters et al.<sup>8</sup> have reported nitrene group transfer from structurally characterized late-transition-metal nitrene complexes (iron and cobalt, respectively) to CO to yield ArNCO. There is considerable interest in phosgene-free processes for the production of isocyanates from nitroaromatics (nitrenes are proposed as intermediates) using late-transition-metal catalysts.<sup>5,9</sup> For example, Moiseev et al.

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reported the production of phenyl isocyanate from nitrobenzene through the use of a palladium cluster catalyst; nitrenes were implicated as intermediates in this transformation.<sup>10</sup> Liu et al. discuss the formation of ArNCO from alkyl-nitro complexes by a copper zeolite catalyst.<sup>11</sup> Kober et al. report the formation of halogenated ArNCO from halogenated nitroaromatics using a catalyst that is 5% PdCl<sub>2</sub> and 5% CuCl<sub>2</sub> supported on SiC.<sup>12</sup>

Although an isolated copper nitrene complex has not been reported, there are structurally characterized examples of copper(I) amido complexes, which could conceivably be viewed as precursors to a copper nitrene. Many copper amido complexes contain chelating amide ligands<sup>13</sup> or adopt dinuclear,<sup>14</sup> trinuclear,<sup>15</sup> or tetranuclear<sup>15,16</sup> structures with bridging amide groups. Recently, a monomeric copper(I) anilido system with a bulky bis(phosphine) ligand has been successfully synthesized and characterized.<sup>17</sup> Warren and co-workers have recently isolated a nitrene bound between two copper  $\beta$ -diketiminato moieties.<sup>18</sup> These researchers further propose an equilibrium between the bridging dicopper nitrene and a terminal copper nitrene complex. Given the long-standing interest of our group in multiply bonded species,<sup>19</sup> we undertook an analysis of the bonding, structure, and reactivity of copper nitrenes because such species have intrigued synthetic chemists in terms of their putative intermediacy in nitrene transfer catalysis.<sup>1</sup>

## Computational Methods

B3LYP<sup>20,21</sup> geometry optimization utilized the *Gaussian03*<sup>22</sup> suite of programs. Complete active space self-consistent-field (CASSCF)<sup>23</sup> calculations were carried out with the *GAMESS* package.<sup>24</sup> Hybrid quantum mechanical/molecular mechanical (QM/MM) calculations employed the *SIMOMM* scheme,<sup>25</sup> integrated in *GAMESS* with the *TINKER* module.<sup>26</sup> The QM part was treated

with the CASSCF approach, while the MM part involved the MM3 force field.<sup>27</sup> The active space employed for the CASSCF calculations is discussed below in section 2. Stevens' effective core potentials (ECPs) and valence basis sets were employed.<sup>28</sup> Main-group basis sets were augmented with d polarization functions. This basis set combination, termed SBKJC(d), has been used extensively in our laboratory in conjunction with a wide variety of wavefunction- and DFT-based methodologies and applied to ground states, excited states, and transition states for metals from across the entire transition series. Vibrational frequencies were calculated at all DFT-optimized stationary points to confirm them as minima. Modeling of triplet species with DFT employed unrestricted Kohn-Sham methods.

## Results and Discussion

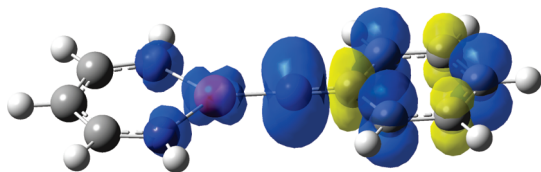
Copper nitrene complexes are proposed as key intermediates in copper-catalyzed nitrene transfer. Furthermore, isolated nitrenes of late transition metals such as Fe,<sup>7,8</sup> Co,<sup>8</sup> and Ni<sup>6,29</sup> are known to transfer NR to CO to yield isocyanates. Given their importance and experimental scarcity, we undertook a proactive investigation of the bonding in copper nitrene complexes. Models with phenyl nitrene (NPh) as a ligand were studied. Borden and co-workers<sup>30</sup> have published extensively on the bonding and reactivity of NPh. The choice of  $\beta$ -diketiminato ligands as a supporting ligand system was motivated by recent experimental work from the Warren,<sup>31</sup> Gunnoe,<sup>32</sup> and Holland<sup>33</sup> groups. Moreover, Ghosh and co-workers have published a very interesting series of papers on 3d metal nitrenes using  $\beta$ -diketiminato supporting ligation.<sup>34</sup>

The copper-containing portion (L'Cu, where L' is the parent  $\beta$ -diketiminato anion, C<sub>3</sub>N<sub>2</sub>H<sub>5</sub><sup>-</sup>) of the nitrene models is formally a closed-shell d<sup>10</sup> Cu<sup>I</sup> ion, and hence a singlet ground state is expected for L'Cu (a supposition supported by DFT calculations). For PhN, a singlet (<sup>1</sup>A<sub>2</sub>)/triplet (<sup>3</sup>A<sub>2</sub>) splitting of ~18 kcal/mol is derived from a combination of multiconfiguration calculations and experiment.<sup>30</sup> The ground state of PhN is a triplet. Note that the <sup>1</sup>A<sub>2</sub> state is an open-shell singlet. There is a closed-shell singlet (<sup>1</sup>A<sub>1</sub>) state of PhN that is calculated to be ~40 kcal/mol above the <sup>3</sup>A<sub>2</sub> ground state.<sup>30</sup>

Given the chemical bonding of its L'Cu and NPh constituents, it is imperative to (a) address whether copper

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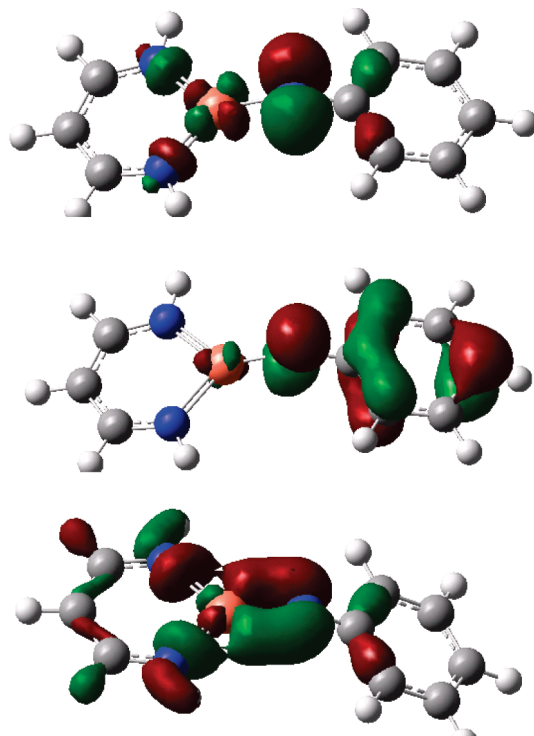


**Figure 1.** Spin density of ( $\beta$ -diketiminate)Cu(NPh). Color code: blue, positive spin density; yellow, negative spin density.

nitrenes possess a singlet or triplet ground state and (b) compare open- and closed-shell bonding descriptions of the singlet states of copper nitrenes. The ground state is of significance with respect to catalysis, particularly amination of C–H bonds. Using known carbenoid chemistry as a model, triplet/singlet copper nitrene complexes may be expected to favor radical abstraction/concerted insertion pathways. The copper nitrene ground spin state will, of course, depend on the nature and strength of the copper–nitrene bond. While a copper(III) imido (i.e., formally  $\text{NR}^{2-}$ ) description seems inconsistent with the group-transfer chemistry of copper aziridination catalysts, any degree of covalent bonding in the Cu(NAr) linkage may shift the energetic balance away from a triplet and toward a singlet ground state.<sup>35</sup> Conversely, a triplet copper nitrene complex is expected to result from a weaker, less covalent copper–nitrene bond. However, given the intricate multireference character revealed by Borden and co-workers<sup>30</sup> for metal-free NPh, quantitative calculations on copper nitrenes are essential to support/refute such predictions. Given the steady progression in research on 3d late-transition-metal nitrene complexes from Fe  $\rightarrow$  Co  $\rightarrow$  Ni, the time seems most propitious for a proactive computational chemistry study of copper nitrene complexes.

**1. DFT Calculations.** A DFT and CASSCF analysis was conducted of ( $\beta$ -diketiminate)Cu(NPh). The latter method, although computationally much more expensive than DFT, was deemed prudent in light of results by Borden et al. on NPh.<sup>30</sup> We begin by discussing the results of the DFT calculations.

**1.1. Triplet State.** A B3LYP/CEP-31G(d) geometry optimization of triplet  $L'\text{Cu}(\text{NPh})$  ( $C_1$  symmetry) yields a minimum with a linear nitrene coordination mode; the Ph substituent is coplanar to the  $\beta$ -diketiminate ligand ( $\text{Cu}-\text{N}_{\text{nitrene}} = 1.779 \text{ \AA}$ ;  $\text{N}_{\text{nitrene}}-\text{C}_{\text{ipso}} = 1.331 \text{ \AA}$ ;  $\text{Cu}-\text{N}_{\text{nitrene}}-\text{C}_{\text{ipso}} = 180.0^\circ$ ). Unrestricted DFT computations on  $^3L'\text{CuNPh}$  indicate delocalized spin density. Spin polarization effects are substantial, as can be seen from large negative spin densities on the ipso and meta carbons of the phenyl substituent (Figure 1) in addition to positive spin densities on the ortho and para carbons. Interactions of  $\pi$  type between the nitrene nitrogen and aryl substituents are also reflected in the short  $\text{N}_{\text{nitrene}}-\text{C}_{\text{ipso}}$  distances.<sup>30</sup> This delocalization suggests the potential for substantial control of copper nitrene reactivity through the choice of functional groups on the aryl substituent, which is inherently reasonable given the synthetic control observed for copper-catalyzed



**Figure 2.** Frontier orbitals of singlet ( $\beta$ -diketiminate)Cu(NPh): LUKSO (top), HOKSO (middle), and HOKSO-3 (bottom).

aziridinations with a variety of nitrene precursors, including Chloramine-T, iodonium imides (e.g.,  $\text{PhI}=\text{NTs}$ ), aryl azides ( $\text{ArN}_3$ ), and so forth.<sup>36</sup>

**1.2. Singlet State.** A singlet state for  $L'\text{Cu}(\text{NPh})$  ( $C_1$  symmetry) was also geometry-optimized by DFT methods and yielded a minimum with a bent nitrene geometry ( $\text{Cu}-\text{N}_{\text{nitrene}} = 1.726 \text{ \AA}$ ;  $\text{N}_{\text{nitrene}}-\text{C}_{\text{ipso}} = 1.356 \text{ \AA}$ ;  $\text{Cu}-\text{N}_{\text{nitrene}}-\text{C}_{\text{ipso}} = 147.8^\circ$ ). The singlet state is calculated to be 13.9 kcal/mol higher in energy than the corresponding triplet state discussed in section 1.1. For  $L'\text{Cu}(\text{NPh})$ , the singlet is approximately  $C_s$  symmetry. Unlike the triplet, the singlet copper nitrene shows some evidence of Cu–N multiple bonding (Figure 2, bottom). Like the triplet, there is delocalization of the nitrene  $p\pi$  orbital onto the aryl substituent (Figure 2, middle).

**2. CASSCF Calculations. 2.1.  $C_{2v}$ -Symmetric Copper Nitrene Model Complexes.** The CASSCF and DFT calculations yield different viewpoints of the copper nitrene electronic structure, in particular singlet states. Several CASSCF active space sizes were investigated, and the results were found to be similar; i.e., the frontier  $b_1$  and  $b_2$   $\pi$  orbitals of the copper–nitrene linkage are the most strongly correlated orbitals. Hence, the discussion focuses on the results from the largest active space studied. The 10-orbital, 10-electron basis set was chosen to incorporate electron correlation effects from the four highest energy doubly occupied orbitals that subtend the  $a_1 + a_2 + b_1 + b_2$  representations, and the four lowest energy unoccupied orbitals that span the

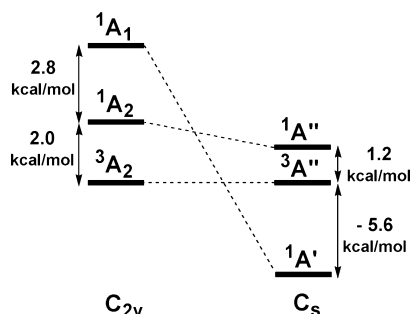
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**Table 1.** CASSCF(10,10)/CEP-31G(d)-Optimized  $C_{2v}$  Geometries for ( $\beta$ -Diketiminato)Cu(NPh)<sup>a</sup>

state	$E_{\text{rel}}$ (kcal/mol)	Cu–N (Å)	N–C <sub>ipso</sub> (Å)	Cu–N–C <sub>ipso</sub> (deg)
$^3A_2$	0.0	1.866	1.368	180.0
$^1A_2$	2.0	1.880	1.364	180.0
$^1A_1$	4.8	1.810	1.341	180.0
$^3A_1$	14.2	1.890	1.308	180.0

<sup>a</sup> Calculations were carried out with the phenyl substituent perpendicular to the plane of the  $\beta$ -diketiminato ligand because this was indicated to be the most stable conformer from DFT calculations.

**Figure 3.** Qualitative correlation diagram for low-energy singlet and triplet states of L'Cu(NPh) in  $C_{2v}$  (left) and  $C_s$  (right) symmetry.

same representations, plus the singly occupied  $b_1$  and  $b_2$  of the Hartree–Fock reference wave function. It is worth noting that basis set requirements for wave-function-based correlated methods are likely to be more stringent than those for DFT but that disk space/memory issues constrained us to use of the SBKJ(d) basis sets. While this will likely change the specific energetics, the essential chemistry of the copper nitrenes vis-à-vis the singlet/triplet splitting and the multi-reference nature of the singlet ground state is not expected to be altered.

CASSCF/CEP-31G(d) geometry optimizations with a 10-orbital, 10-electron active space were first carried out under  $C_{2v}$  symmetry for singlet and triplet ( $\beta$ -diketiminato)Cu(NPh) for all possible state symmetries. The CASSCF(10,10) calculations yield a  $^3A_2$  ground state within the constraint of  $C_{2v}$  symmetry. Low-energy  $^1A_1$ ,  $^1A_2$ , and  $^3A_2$  states were also obtained. Singlet and triplet states of  $B_1$  and  $B_2$  symmetry were much higher in energy ( $>73$  kcal/mol). The  $^3A_2$  state obtained by CASSCF geometry optimization of L'Cu(NPh) is reminiscent of the ground-state triplet found by DFT calculations (vide supra). Furthermore, Borden et al. have concluded from experimental and computational data that the ground state of PhN is  $^3A_2$ , which is  $\sim 18$ – $20$  kcal/mol below the lowest-energy singlet state ( $^1A_2$ ) of NPh.<sup>30</sup> Hence, the  $^3A_2$  ( $\beta$ -diketiminato)Cu(NPh) state is conceptually the product of the  $^3A_2$  NPh and  $^1A_1$  ( $\beta$ -diketiminato)Cu states of its constituents. Pertinent structural data for  $C_{2v}$  nitrene complexes are summarized in Table 1.

The singlet ( $^1A_2$ )/triplet ( $^3A_2$ ) splitting at the CASSCF level of theory, i.e., 2.0 kcal/mol [Figure 3 (left-hand side)], is considerably less than that indicated by DFT calculations. The lowest singlet  $^1A_1$  is now calculated to be only 4.8 kcal/mol higher in energy than the  $^3A_2$  state of ( $\beta$ -diketiminato)-Cu(NPh) for CASSCF/CEP-31G(d) geometries optimized within the constraint of  $C_{2v}$  symmetry. Hence, CASSCF calculations greatly stabilize both the open-shell ( $^1A_2$ ) and

**Table 2.** CASSCF(10,10)/CEP-31G(d)-Optimized  $C_s$  Geometries for ( $\beta$ -Diketiminato)Cu(NPh)<sup>a</sup>

state	$E_{\text{rel}}$ (kcal/mol)	Cu–N (Å)	N–C <sub>ipso</sub> (Å)	Cu–N–C <sub>ipso</sub> (deg)
$^1A'$	0.0	1.852	1.396	132.0
$^3A''$	5.6	1.843	1.335	179.7
$^1A''$	6.8	1.851	1.332	180.0
$^3A'$	11.7	1.994	1.401	124.1

<sup>a</sup> CASSCF calculations were carried out with the phenyl substituent perpendicular to the  $C_s$  plane of the molecule because this conformation was found to be most stable in DFT geometry optimization.

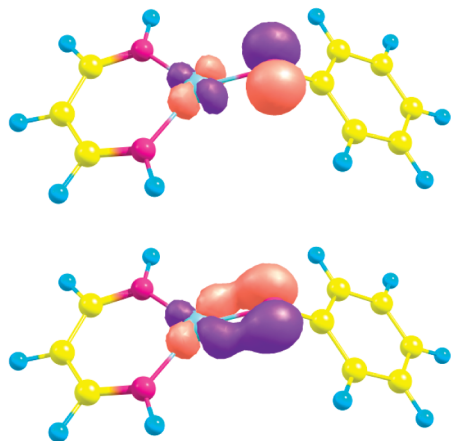
closed-shell ( $^1A_1$ ) singlet states of the copper nitrene relative to the triplet state, suggesting that the former possess significant multi-reference character.

## 2.2. $C_s$ -Symmetric Copper Nitrene Model Complexes.

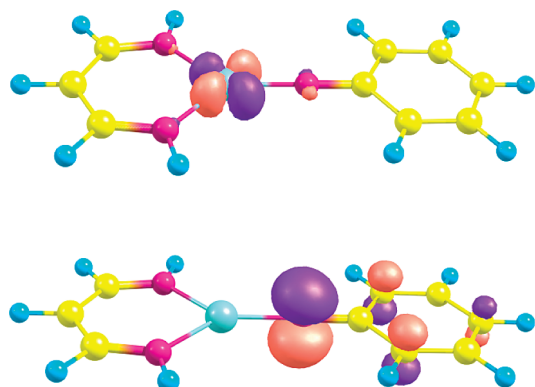
The singlet/triplet energy splitting obtained for  $C_{2v}$  model geometries of L'Cu(NPh) is likely to be less than the foregoing estimates because the DFT evidence (see section 1.2) suggests that singlet copper nitrenes have an appreciably more bent nitrene coordination mode than the corresponding triplets. For this reason, utilizing the 10-orbital, 10-electron CASSCF methodology, ( $\beta$ -diketiminato)Cu(NPh) was optimized under  $C_s$  symmetry for singlet and triplet states of both  $A'$  and  $A''$  symmetry. When bending of the nitrene ligand is permitted, the closed-shell  $^1A'$  state is now predicted to be the ground state for L'Cu(NPh). Relative energies (kcal/mol) of the other symmetry states are 6 ( $^3A''$ ), 7 ( $^1A''$ ), and 12 ( $^3A'$ ) (Figure 3). While the  $A'$  states are bent (Table 2), the  $A''$  states return to linear nitrene coordination ( $150^\circ$  was used as a starting guess for the geometry optimizations as a compromise between sp and  $sp^2$  hybridization of the nitrene nitrogen) and thus  $^3A''$  and  $^1A''$  correspond to the  $^3A_2$  and  $^1A_2$  states of  $C_{2v}$  L'Cu(Ph), respectively (see Figure 3).

As with multi-reference calculations on NPh,<sup>30</sup> variations are seen in the CASSCF-optimized bond lengths between the ipso carbon and the nitrene nitrogen (Table 2) for the different electronic states. Furthermore, interesting variations are also seen in copper–nitrene nitrogen bond distances and copper–nitrene–ipso carbon bond angles for the different symmetry states of  $C_s$  ( $\beta$ -diketiminato)Cu(NPh). The lowest-energy singlet ( $^1A'$ ) and triplet ( $^3A''$ ) states of CASSCF(10,10)/CEP-31G(d)-optimized L'Cu(NPh) are bent and linear, respectively, a result consistent with the DFT geometry optimizations of these nitrenes. Apart from the high-energy  $^3A'$  state, Cu–N bonds to the nitrene are little changed from 1.84 to 1.85 Å (Table 2) for the different electronic states. The nitrene nitrogen–ipso carbon distance for the  $^1A'$  ground state is  $\sim 0.06$  Å longer than the analogous bond in the  $^3A''$  state. Indeed, both  $A'$  states have longer N–C<sub>ipso</sub> bond lengths than the  $A''$  states, regardless of the spin state.

One important result that emerges from the present calculations is that the  $^1A'$  ground state cannot be adequately described by a single electronic configuration, as evidenced by the computed natural orbital occupation numbers (NOONs) of  $(\pi_{\text{CuN}})^{1.5}(\pi_{\text{CuN}^*})^{0.5}$  (Figure 4). These values are far removed from the single determinant occupation numbers of 2 and 0, respectively, and suggest significant diradical character to the copper–nitrene  $\pi$  bond. Analysis of the natural orbitals from the CASSCF calculation of  $^1A'$  ( $\beta$ -diketiminato)-



**Figure 4.**  $\pi_{\text{CuN}}$  (bottom) and  $\pi_{\text{CuN}^*}$  (top) natural orbitals for the  $^1A'$  state of  $(\beta\text{-diketiminate})\text{Cu}(\text{NPh})$ . The NOONs are  $1.5 e^-$  for  $\pi_{\text{CuN}}$  and  $0.5 e^-$  for  $\pi_{\text{CuN}^*}$ .

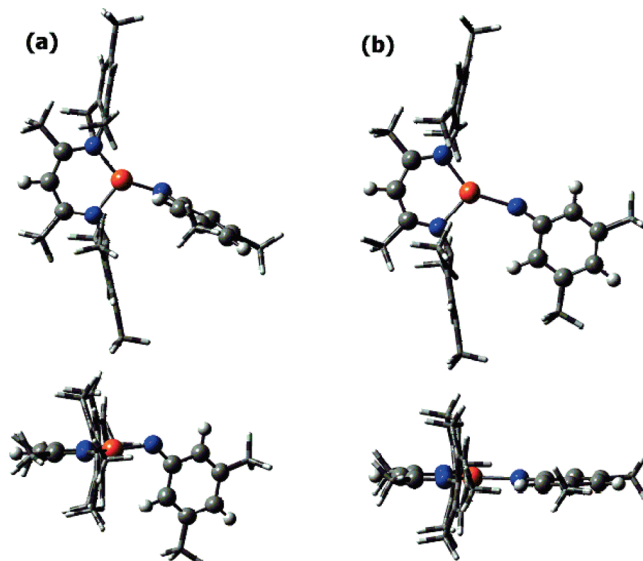


**Figure 5.**  $\pi_{\text{N}}$  (bottom) and  $\pi_{\text{Cu}}$  (top) natural orbitals for the  $^3A''$  state of  $(\beta\text{-diketiminate})\text{Cu}(\text{NPh})$ . The NOONs are  $\sim 1.0 e^-$  for both.

$\text{Cu}(\text{NPh})$  supports some degree of multiple bonding character for the copper–nitrene bond (Figure 4).

The  $A''$  ( $\sim A_2$ ) states (both singlet and triplet) of  $(\beta\text{-diketiminate})\text{Cu}(\text{NPh})$  are quite different in their character from the corresponding  $A'$  states of  $\text{L}'\text{Cu}(\text{NPh})$ , the former displaying perpendicular  $\pi$  symmetry orbitals that are highly polarized on either the copper or nitrene nitrogen end (Figure 5). In this regard, the description of the copper–nitrene bond of  $^3A''$   $(\beta\text{-diketiminate})\text{Cu}(\text{NPh})$  within the CASSCF framework is reminiscent of similar calculations on dioxygen.<sup>37</sup> The nitrene nitrogen-polarized orbital remains partially delocalized to the phenyl substituent [Figure 5 (bottom)].

**3. QM/MM Calculations.** With regards to possible steric effects, bulky substituents were added to the  $\beta\text{-diketiminate}$  ligand: two mesityl and two methyl substituents ( $\text{L}^{\text{Me,Mes}}$ ), while the nitrene substituent was set as 3,5-dimethylphenyl.<sup>38</sup> These modifications model the putative terminal copper nitrene intermediate recently reported by Warren and co-workers.<sup>18</sup> Figure 6 depicts the optimized structures of singlet ( $^1A$ ) and triplet ( $^3A$ ) states using the hybrid CASSCF(10,10)/CEP-31G(d):MM3 method with no symmetry constraint to the geometry optimization.



**Figure 6.** Top (top) and side (bottom) views of  $(\text{L}^{\text{Me,Mes}})\text{Cu}(\text{N-3,5-C}_6\text{H}_3\text{Me}_2)$  optimized geometries using a QM/MM approach. The QM region [CASSCF(10,10)/CEP-31G(d)] is illustrated in a ball-and-stick representation, while the MM region (MM3 force field) is illustrated in a stick representation: (a) singlet state; (b) triplet state.

Optimized geometries of  $(\text{L}^{\text{Me,Mes}})\text{Cu}(\text{N-3,5-C}_6\text{H}_3\text{Me}_2)$  using hybrid QM/MM methods show the same structural patterns as those for smaller models: the triplet is closer to linear ( $\text{Cu-N}_{\text{nitrene}}-\text{C}_{\text{ipso}} = 160.7^\circ$ ), while the singlet is markedly bent ( $\text{Cu-N}_{\text{nitrene}}-\text{C}_{\text{ipso}} = 130.4^\circ$ ). Still, the singlet/triplet energy splitting of 21.5 kcal/mol is larger than those in previous small-model calculations (Table 2), suggesting a less favorable steric interaction between the nitrene and  $\text{Cu}(\beta\text{-diketiminate})$  substituents in the triplet state versus the singlet ground state. The NOONs for the singlet  $(\text{L}^{\text{Me,Mes}})\text{Cu}(\text{N-3,5-C}_6\text{H}_3\text{Me}_2)$  are very similar to those obtained for the  $^1A'$  ground state of  $\text{L}'\text{Cu}(\text{NPh})$ , i.e.,  $1.5 e^-$  and  $0.5 e^-$  for natural orbitals akin to those shown in Figure 4 for the  $\text{L}'\text{Cu}(\text{NPh})$  model. However, in the case of the triplet  $(\text{L}^{\text{Me,Mes}})\text{Cu}(\text{N-3,5-C}_6\text{H}_3\text{Me}_2)$ , the natural orbitals show that both  $p\pi$  orbitals of the nitrene nitrogen are occupied with  $\sim 1 e^-$  each. Thus, the QM/MM calculations suggest that the increase of steric effects on the  $\beta\text{-diketiminate}$  ligand will tend to destabilize the triplet relative to the ground-state singlet of copper nitrenes with these specific supporting ligands and substituents.

## Summary and Conclusions

Copper nitrene complexes are of considerable interest as intermediates in nitrene transfer although they have thus far, to our knowledge, eluded structural characterization. Thus, DFT, CASSCF, and QM/MM methods were employed in conjunction with ECP basis sets to study such species. The copper nitrene complexes studied are of the form  $(\beta\text{-diketiminate})\text{Cu}(\text{NPh})$ ,<sup>31–33,38</sup> and two models were considered. The “small” model [ $\text{L}'\text{Cu}(\text{NPh})$ ], where all substituents on the  $\beta\text{-diketiminate}$  and phenyl groups are replaced with H atoms, was investigated under both  $C_{2v}$  and  $C_s$  symmetries. The larger model [ $(\text{L}^{\text{Me,Mes}})\text{Cu}(\text{N-3,5-C}_6\text{H}_3\text{Me}_2)$ ] possesses methyl and mesityl substituents on  $\beta\text{-diketiminate}$

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and a 3,5-dimethylphenyl substituent on the nitrene nitrogen. Of primary interest in this research is whether the electronic ground state of these copper nitrenes is singlet or triplet and the nature of the bonding character between the copper and nitrene.

While DFT calculations suggest a triplet ground state for  $L'Cu(NPh)$ , more expensive CASSCF methods on  $L'Cu(NPh)$  and QM/MM calculations on  $(L^{Me,Mes})Cu(N-3,5-C_6H_3Me_2)$  indicated a singlet ground state. In all cases, singlets are found to possess a bent geometry around nitrene nitrogen. Singlet copper nitrene electronic states are highly multireference in their compartment, as indicated by NOONs of  $(\pi_{CuN})^{1.5}(\pi_{CuN}^*)^{0.5}$ , and thus their description via single-determinant methods must be called into question. Hence, it is not surprising that the description of the  $^1A'$  state is tenuous by single-determinant methods, even a correlated technique such as DFT.

The triplet states of  $(\beta$ -diketiminato) $Cu(NPh)$ , which are low-energy excited states, show a completely different bonding pattern as compared to their singlet congeners. First, triplets are found to possess a linear geometry. Second, the CASSCF calculations on  $L'Cu(NPh)$  indicate that the unpaired electrons reside in highly polarized  $\pi$  orbitals on Cu and  $N_{nitrene}$  atoms. DFT calculations on  $L'Cu(NPh)$  and QM/MM calculations on  $(L^{Me,Mes})Cu(N-3,5-C_6H_3Me_2)$  indicate that the majority of the spin density resides on the nitrene nitrogen with some delocalization of the spin density to the aryl substituent. Regardless, the triplet states of copper nitrenes display minimal evidence of copper–nitrene covalent bonding.

In light of their electronic and molecular structural differences, it is interesting that bent/singlet and linear/triplet copper nitrenes possess CuN bond lengths that differ by a few picometers. We hypothesize that this results from a cancelation of effects; i.e., the shorter Cu–N distance expected from the sp-hybridized nitrogen in linear/triplet  $L'Cu(NPh)$  versus sp<sup>2</sup>-hybridized bent/singlet  $L'Cu(NPh)$  countermands the shortening of the latter from partial multiple bonding character.

The shortened N–C<sub>ipso</sub> bond lengths and delocalization of the  $N_{nitrene}$   $\pi$  orbitals onto the phenyl substituent for both the singlet ground state and low-energy triplet excited state suggest that Cu– $N_{nitrene}$  bonding, and hence their resulting reactivity, may be substantially modified by using various substituted phenyl groups. Similar observations with regard to NAr  $\pi$  delocalization were made in a general study of the more prevalent early-to-middle nitrene/imido complexes.<sup>39</sup>

From the perspective of catalysis, a strong preference for a singlet state can be viewed as desirable because one expects singlet copper nitrenes to be prone to concerted, insertion processes (e.g., amination of C–H bonds), while triplet states may be predisposed to less selective, radical processes. Analysis of wave functions from the CASSCF and QM/MM calculations revealed the existence of a closed-shell singlet, with some degree of multiple bonding character for the copper–nitrene bond. Indeed, in view of previous research on alkylidene/carbene<sup>19,35,40</sup> and imido/nitrene complexes, the singlet ground state for these copper nitrenes is itself an indicator of a substantial degree of copper–nitrene covalent bonding for the singlet states.

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**Supporting Information Available:** Cartesian coordinates for calculated stationary points and a full citation for ref 22. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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